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(21) International Application Number: PCT/FI94/00015 (22) International Filing Date: 12 January 1994 (12.01.94) (30) Priority Data: 930122 12 January 1993 (12.01.93) FI (71) Applicant (for all designated States except US): ENVIRONICS OY [FI/FI]; Työmiehenkatu 2, FIN-50100 Mikkeli (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): PAAKKANEN, Heikki [FI/FI]; Sairaalkatu 5 A 26, FIN-70110 Kuopio (FI). KÄRPÄNOJA, Esko [FI/FI]; Saukonkuja 6 A, FIN-50170 Mikkeli (FI). KÄTTÖ, Tero [FI/FI]; Kaimentie 27 B 26, FIN-50160 Mikkeli (FI). KARHAPÄÄ, Tarmo [FI/FI]; Pellontorpantie 10 B 7, FIN-50100 Mikkeli (FI). OINONEN, Asko [FI/FI]; Piisaminkuja 1 A 10, FIN-50190 Mikkeli (FI). SALMI, Hannu [FI/FI]; Piilopirtintie 3, FIN-50100 Mikkeli (FI). (74) Agent: KEIJO HEINONEN OY; Fredrikinkatu 61A, P.O. Box 671, FIN-00101 Helsinki (FI).		(81) Designated States: CA, JP, NO, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: METHOD AND EQUIPMENT FOR DEFINITION OF FOREIGN MATTER CONTENTS IN GASES		
(57) Abstract <p>The object of the invention is a method for detection of foreign matter contents in gas, in which method the gas is led to a flow channel (1), in which the gas is filtered and heated, whereafter the gas is led to the measuring cells (3). The invention is characterized in that for the analyzing of the gas is used at least one ionization cell and at least one semiconductor cell (3, 6) arranged in parallel or in sequence.</p>		

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METHOD AND EQUIPMENT FOR DEFINITION OF FOREIGN MATTER CONTENTS IN GASES

The invention relates to a method and equipment for definition of foreign matter contents in gas.

Foreign matters are analyzed and their contents are defined to control the quality of the breathing air. When defining from the gas certain toxic components which are toxic already in relatively small quantities, other air components may disturb the detection. The contents of different substances rapidly and reliably in the air, like carbon dioxide, may vary. The detection of different molecules or molecule groups performed from gases in general or from vapor originating from evaporated solid material or liquid matters is often connected with problems. The detection of especially toxic agents in the air, nerve gases diffused in the breathing air, has been a problem due to their small contents. The detections should be made already in a few seconds. The most efficient nerve gases should be detected already at contents of 1/100 ppm.

The most sensitive analysis devices are based on air ionization, e.g. by alpha- or beta radiation and by measuring the ions in different circumstances. In one method the ions so formed are put to migrate through a particular labyrinth and the remaining ions are measured based on the current they cause. Another method analyzes the mobility of the formed ions through certain lattices and finally measures the ion current. These two methods generally detect very heavy molecules from the air, like most of the combat gases. In one method the ionized molecules are led through chambers having different electric fields, after which the current is detected from the measuring electrodes, by which the quality and quantity of the foreign matter molecules are identified.

Such a quick and reliable method is presented in the FI-

patent 75055. To define the foreign matter contents in the gas in this method, the gas and its components are ionized in the ionization zone. They are led into a narrow analyzer channel, in which they due to the capillary effect have to pass in the middle of the channel. From there they are further deflected by electric fields causing unequal voltages to the electrode in the channel border, producing there the ion current. By the current spectrum based on ion currents, the different substances are identified and the ion contents in the gas is defined by comparing them to corresponding spectra obtained from standard samples of the different agents. A solution has also been disclosed, in which the ions contained in the gas are, before measuring, separated in a separator into positive and negative ions, of which the other ones are analyzed.

The DE-patent publication 2028805 discloses a method for detecting trace vapors, which undergo ion-molecule reactions and for separating, concentrating and measuring of molecular quantities of trace substances in gaseous samples. In an electric field essentially parallel to the gas stream between two electrodes arranged in a detecting chamber, the detection and measurement is accomplished by utilizing the difference in velocity or drift time of ions of different mass in the electric field applied to the gas stream. The electric field causes the primary ions to migrate towards a plurality of ion gates provided rectangular to the gas stream and in parallel between the electrodes, during which the primary ions react with molecules of a gas to be detected, converting the molecules to secondary or product ions, thereby measuring and classifying the ions according to the particular mass.

From the EP-publication 21518 is known a method similar to the one above for detecting trace quantities of chemical species defined in a gaseous mixture by ionizing a proportion of the molecules and leading these gas molecules

through an electric field which is arranged in the above manner in a detecting chamber.

The CH-publication 550 399 discloses an air pollution measuring equipment comprising a first and a second air capacitor each having a suitable length through which ionized air containing pollution flows laminarily at a constant velocity. The capacitors may have planar or cylindrical electrodes and may comprise two or more electrodes. In order to provide different electric fields for generating a first and second varying measurement signal as a function of a small and large positive ion concentration in the air stream generated by means of an exhaust fan, the electrodes of the capacitors are supplied with different voltages. The output signals measured via the electrodes of the capacitors are applied to the inputs of dividing and summing circuit means, the output of which provide a final output signal which constitutes a measure of air pollution.

The method and the equipment according to the invention provide a decisive improvement of the above presented methods. The implementation of this with the method and equipment according to the invention is mainly characterized in what is presented in claims 1 and 5.

25

One of the most important advantages of the invention is that the inaccuracy of the analysis due to gas or air moisture can be eliminated. The reliability of the analysis is improved. The sensitivity is great and the response time is short. Other organic substances or solvents or tobacco smoke do not disturb the foreign matter analysis.

In the following the invention is described with reference to the enclosed drawings, in which:

35

Fig. 1 presents a diagram of the measuring equipment of the subject invention.

Fig. 2 presents a diagram of another implementation form of the equipment.

Fig. 1 presents the equipment according to the invention.

5 The gas to be analyzed is sucked into tube 1, filtered with the heatable filter 2 and led into the ionization cell 3, of which can as such be provided several in parallel or in sequence, and which can either be according to the FI patent 75055 or any gas ionization based gas analysis device,
10 whereafter the gas is led to the semiconductor cell, which can be several in parallel or in sequence.

An alternative solution is to place according to fig. 2, the ionization cells and the semiconductor cells parallel in the
15 gas flow, so that the gas is distributed to be analyzed to both cells /battery.

The semiconductor cell can in the solution be any gas sensor based on the reaction between the semiconductor surface and
20 the gas, which as such is based on the known technique. In the equipment according to the invention the signals of all measuring cells are utilized simultaneously for the performance of the gas analysis for calculations and other conclusions for improved separation of gases from each other in
25 different circumstances.

The gas is e.g. charged by the radiation transmitted from the alpha- or beta radiation source 4. The gas is led to a measuring tube 5. In the collection field the field elec-
30 trodes have the voltage V_1, V_2, \dots, V_n . The back-plate voltage is V_r . In the collection field, the light ions charged in the gas, are collected into the field electrodes V_n . In the measuring chamber the further advanced remaining heavy ions cause an ion current I_n to the electrodes in the chamber
35 border, which is registered. From each value I_n , in which n is an integer, e.g. 1-6, is formed a diagram, the form of which depicts the substance to be analyzed. Normally the

electric field of the ionization cell is stronger in the beginning of the chamber and weaker in the collecting zone.

The gas is led further to the semiconductor cell 6, formed of e.g. a tin dioxide (SnO_2) crystal. By changing the doping, a sensitive analyzing device can be obtained for different substances, e.g. for mustard gas. The signals obtained by the above method and the semiconductor cells are gathered together and analyzed together in e.g. a data processor 7.

10 The gas analyzed by the semiconductor cell together, is preferably such a gas, which analyzed as moist, does not give a signal with the above mentioned ionization method but only when measured by the semiconductor cell. An example of such a gas is the mustard gas.

15

The tests for the gas streams having hazardous matter in it have been carried out in different humidities with both the ionization cell and the semiconductor cell mounted sequentially or parallel to each other. The relative humidities

20 were 10, 50 and 90 %. The gas stream was conducted through the channel by a pump. In the table, A corresponds ionization cell and B semiconductor cell, respectively.

The following table shows the results of the tests.

25

Device which responded	Concentration mg/m^3	Humidity %	Response time s
B	0,2	90	1
30 B	0,2	10	9
B	6	90	12
A	6	10	28
B	10	50	9
A	10	10	9

35

The test results show that the presence of the mustard gas will be detected most effectively using the combination of

the ionization and semiconductor cell at low concentrations and at all the relative humidities and especially at the moderate or larger humidities.

5 The invention has been described with reference to only one of its favorable forms of implementation. The solutions presented above and in the drawings are only examples, and the invention is not to be considered as so limited, but all modifications within the scope of the inventive idea are
10 naturally possible.

CLAIMS

1. A method for detection of foreign matter contents in gases in which the gas stream is ionized at the ionizing
5 zone,

ionized gases and materials contained in the gas stream are led through at least one chamber having different electric fields the fields being transverse to the gas stream, so
10 that at least some ions are removed in the collecting zone in the beginning of the chamber,

the electric currents of the ions reaching the measuring zone are measured in the electric field ,

15

receiving the signals and on the basis of the amount and relationship of said signals corresponding to the measured electric currents an analysis of the foreign matter in the gases is provided,

20 characterized in that conducting the analyzing gas stream into at least one ionization cell and at least one semiconductor cell arranged in parallel and/or in sequence to each other.

25 2. A method for detection of foreign matter contents in gas, in which the gas is led to a flow channel, in which the gas is filtered and heated, whereafter the gas is led to measuring cells, characterized in that for the analyzing the gas is conducted to at least one ionization cell and at
30 least one semiconductor cell arranged in parallel and/or in sequence.

3. A method according to claim 1 or 2, characterized in that for the analyzing of the gas in different circumstances
35 the signals of the ionization cells and semiconductor cells arranged in parallel or in sequence are utilized simultaneously.

4. A method according to one or more of the above claims,
characterized in that the gas is charged and led to a flow
channel, the light ions of the gas are removed in the col-
lection field, and the field currents caused by the heavy
5 ions of the gas are registered.

5. A method according to one or more of the above claims,
characterized in that the same gas is further led to the
semiconductor cell to detect the presence of some particular
10 substance.

6. An equipment for detection of foreign matter contents in
gas, which equipment comprises a flow channel for leading
gas to the same, gas filtering and heating devices and
15 measuring cells, characterized in that the measuring
cells used for the gas analysis comprise at least one ion-
ization cell and at least one semiconductor cell arranged in
parallel or in sequence.

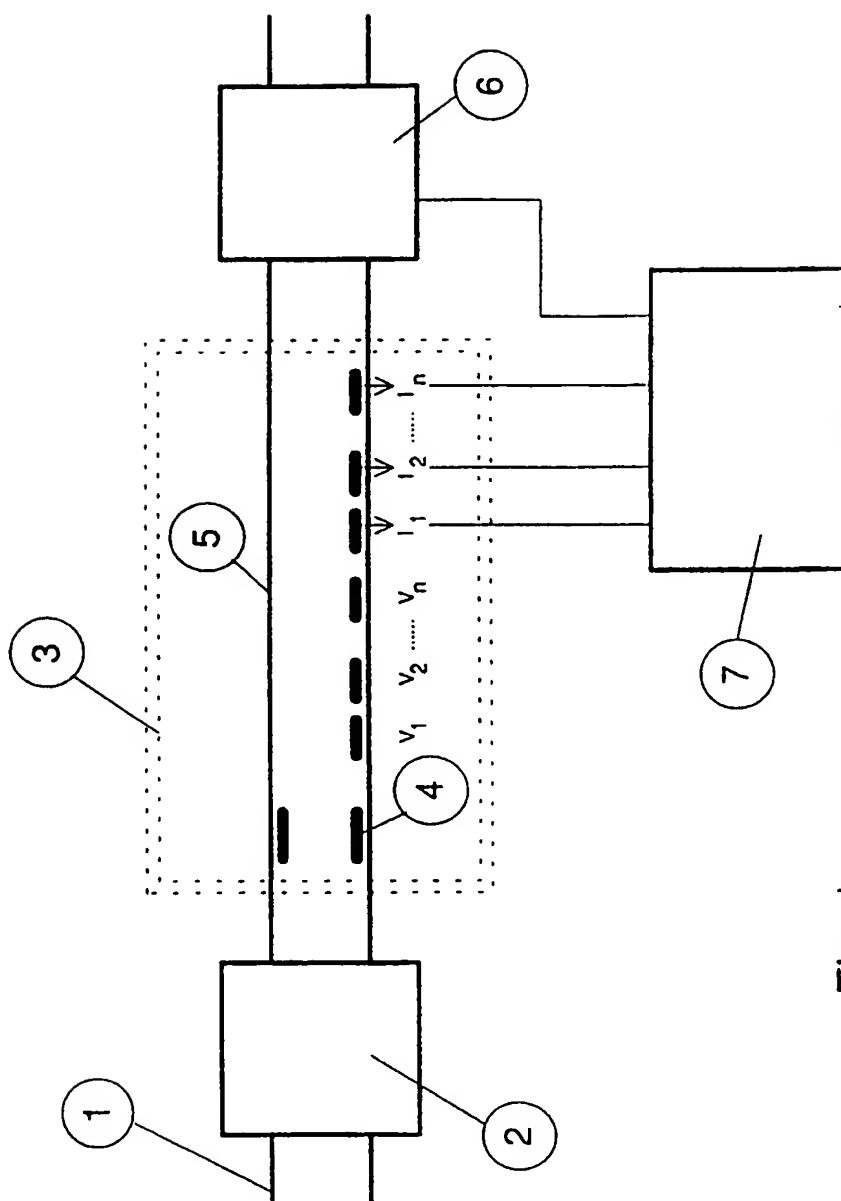


Fig. 1

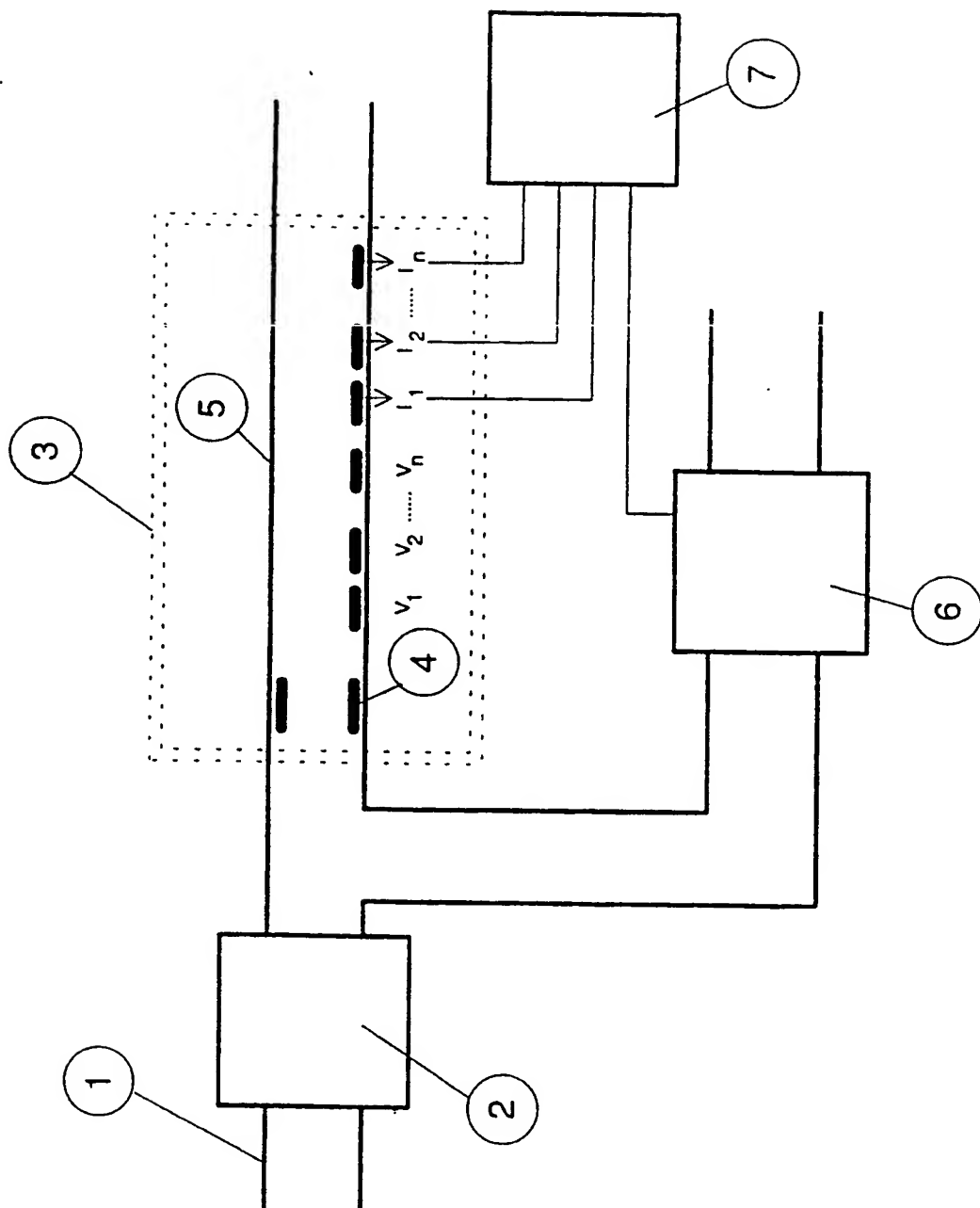


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 94/00015

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: G01N 27/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO, A1, 9210751 (LEHMANN, MARTIN), 25 June 1992 (25.06.92), page 23, line 22 - page 25, line 3; page 30, line 23 - page 31, line 20, figures 5,8, claims 17,18 --	1-6
A	DE, A1, 3342230 (VEB KOMBINAT ROBOTRON), 23 August 1984 (23.08.84), page 4, line 12 - line 35, figure 1, claim 1 --	1-6
A	US, A, 5047723 (PERTTI PUUMALAINEN), 10 Sept 1991 (10.09.91), figure 1, claims 1-2 -- -----	1-6

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

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Information on patent family members

26/02/94

International application No.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9210751	25/06/92	AU-A- 8914491 AU-A- 8928291 CN-A- 1063061 DE-A- 4038993 EP-A- 0513276	08/07/92 08/07/92 29/07/92 11/06/92 19/11/92
DE-A1- 3342230	23/08/84	NONE	
US-A- 5047723	10/09/91	AU-B- 605770 AU-A- 7517787 CA-A- 1304836 DE-D,T- 3787281 EP-A,B- 0308420 SE-T3- 0308420	24/01/91 11/01/88 07/07/92 05/01/94 29/03/89